

FEDERAL REPUBLIC OF
GERMANYGERMAN PATENT
OFFICE

12. UNEXAMINED PATENT APPLICATION

11. DE 41 31 576 A1

51. Int. Cl.⁵:

C 07 C 17/38

C 07 C 17/34

C 07 C 17/158

C 07 C 18/045

21. Case No.:

P 41 31 576.5

22. Application date:

September 23, 1991

43. Date application published:

March 25, 1993

71. Applicant:

Hoechst AG, 8230 Frankfurt, DE

72. Inventor:

Winhold, Michael, Dipl.-Ing. Dr., 5024 Pulheim, DE;
Perkow, Helmut, Dipl.-Chem. Dr., 5030 Hürth, DE;
Link, Gerhard, Dipl.-Ing., 5500 Mainz, DE;
Schwarzmaier, Peter, Dipl.-Ing., 8261 Kastl, DE;
Krumböck, Reinhard, Dipl.-Ing.; Kühn, Wenzel,
Dipl.-Chem. Dr., 8269 Burgkirchen, DE

54. Utilization of the heat of 1,2-dichloroethane vapors

57. This invention relates to a method for the utilization of the heat of 1,2-dichloroethane vapors as they occur in a zone for the separation of high boiling point compounds, in which the high boiling point fractions are extracted from crude 1,2-dichloroethane in the form of a mixture with liquid 1,2-dichloroethane, and the crude 1,2-dichloroethane in aqueous form originates from a dehydration zone of an oxychlorination plant and from a vinyl chloride distillation zone of a 1,2-dichloroethane plant for the production of vinyl chloride, and is characterized in that the vaporizer of the zone for the separation of high boiling point compounds is operated with the reaction enthalpy of the direct chlorination of ethylene into 1,2-dichloroethane and the 1,2-dichloroethane vapors are divided into 3 gas streams:

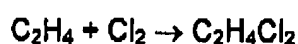
- a) a first gas stream is transported to the vaporizer of a vacuum distillation zone, in which 1,2-dichloroethane is separated from high boiling point compounds, and the condensate that is formed in the vaporizer is collected in a 1,2-dichloroethane reservoir;
- b) a second gas stream leads into a condensation zone and the condensate formed collects in the 1,2-dichloroethane reservoir;
- c) a third gas stream is compressed in a compression zone and in this state is fed to a vaporizer of the dehydration zone in which low boiling point compounds and water are added to the 1,2-dichloroethane from oxychlorination plants and the condensate that is formed collects in the 1,2-dichloroethane reservoir.

Description

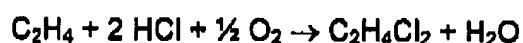
This invention relates to a method for the utilization of the heat of 1,2-dichloroethane vapors as they occur in a zone for the separation of high boiling point compounds in which the high boiling point compounds are extracted in liquid form from crude 1,2-dichloroethane and the raw 1,2-dichloroethane originates in dehydrated form from a dehydration zone of an oxychlorination plant and from a vinyl chloride distillation zone of a 1,2-dichloroethane cracking plant for the production of vinyl chloride.

In "Vinyl Chloride and PVC Manufacture", Marshall Sittig, Noyes Data Corporation, Noyes Building, Park Ridge, NY 07656 (1978), pages 6 to 91, potential methods in which vinyl chloride can be produced from ethylene and chlorine in a direct chlorination, oxychlorination and 1,2-dichloroethane cracking in a compound method are described.

The vinyl chloride production in this compound method is coupled with the consumption of large quantities of energy. The main quantities of energy are consumed during the cracking of the 1,2-dichloroethane and in the purification stages. On the other hand, greater reaction enthalpies are released during the direct chlorination of



and during the oxychlorination of



Therefore there has been no shortage of proposals regarding the utilization of these energies.

In DE-A-29 13 004, the heat of the fission gas is utilized in the purification stages for the operation of the vaporizer in the distillation operations. One disadvantage of this method is that it is that the heat that is released at a high temperature level is consumed on a low temperature level, and the reaction enthalpies that occur on a low temperature level are not used for direct chlorination and oxychlorination.

In EP-A-00 75 742, the reaction enthalpy of the direct chlorination is used for the purification of 1,2-dichloroethane.

EP-B-01 80 925 teaches a method for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane in which the energy utilization is improved by compressing the vapors from the high boiling point column and then condensing and cooling them in the vaporizer of the high boiling point column. One disadvantage of this method is the high boiler temperature in the high boiling point column of 120 to 135°C, as a result of which a more rapid contamination of the high boiling point column by cracking products is inevitable. The reaction enthalpy of the direct chlorination of ethylene cannot be used on account of the high boiler temperature of the high boiling point column. If the temperature in the direct chlorination reactor were to be increased accordingly, an increased formation of byproducts would be inevitable.

The object of the invention is therefore to describe a method with which the reaction enthalpy of the direct chlorination can be used on a low temperature level and the sump temperatures in the high boiling point separation zone can be kept low enough that the formation of cracking products is reduced and an effective 1,1,2 trichloroethane separation is achieved.

Specifically, the invention relates to a method for the utilization of the heat of 1,2-dichloroethane vapors as they occur in a high boiling point separation zone in which the high boiling point fractions are extracted in liquid form from crude 1,2-dichloroethane in the form of a mixture with 1,2-dichloroethane, and the crude 1,2-dichloroethane in dehydrated form originates from a dehydration zone of an oxychlorination plant and from a vinyl chloride distillation zone of a 1,2-dichloroethane cracking plant for the production of vinyl chloride, which is characterized in that the vaporizer of the high boiling point separation zone is operated with the reaction enthalpy of the direct chlorination of ethylene to 1,2-dichloroethane and divides the 1,2-dichloroethane vapors into 3 gas streams:

- a) a first gas stream is transported to the vaporizer of a vacuum distillation zone, in which 1,2-dichloroethane is separated from high boiling point compounds, and the condensate that is formed in the vaporizer is collected in a 1,2-dichloroethane reservoir;

- b) a second gas stream leads into a condensation zone and the condensate formed collects in the 1,2-dichloroethane reservoir;
- c) a third gas stream is compressed in a compression zone and in this state is fed to a vaporizer of the dehydration zone in which low boiling point compounds and water are added to the 1,2-dichloroethane from oxychlorination plants and the condensate that is formed collects in the 1,2-dichloroethane reservoir.
- d) optionally, from the third gas stream, downstream of the compression zone, a partial gas stream branches off into the vaporizer of a hydrochloric acid distillation zone in which hydrochloric acid is distilled from a mixture of vinyl chloride and 1,2-dichloroethane.

The method claimed by the invention can preferably and optionally be characterized in that:

- 1. the sump of the high boiling point separation zone is held at a temperature of 95 to 120°C and a vapor temperature of 84 to 112°C is established;
- 2. the 1,2-dichloroethane vapors of the third gas current are compressed at a pressure of 2 to 4.5 bar, whereby a temperature of 110°C to 150°C is established;
- 3. 3 to 15%, in particular 5 to 10% of the 1,2-dichloroethane vapors are condensed in the condensation zone;
- 4. a reflux of $R = 0.2$ to 0.8 , in particular of $R = 0.4$ to 0.6 , is established in the high boiling point fraction separation zone;
- 5. the high boiling point fractions are extracted from the boiler of the vacuum distillation zone from the sump product of the high boiling point fraction separation zone in the vacuum distillation zone at a sump temperature of 75 to 100°C and a boiler pressure of 0.25 to 0.6 bar;
- 6. the dehydrated crude 1,2-dichloroethane is extracted from the boiler of the dehydration zone at a sump temperature of 95 to 115°C and a boiler pressure of 1.5 to 2.5 bar, and introduced into the high boiling point fraction separation zone.

The method claimed by the invention is explained in greater detail in the attached schematic drawing.

Via the line 13, crude 1,2-dichloroethane of the type that occurs after separation of the hydrochloric acid and vinyl chloride from the cracked gas of a 1,2-dichloroethane cracking plant and via the line 14 crude 1,2-dichloroethane, as it occurs after the dehydration column 2 of an oxychlorination plant, are introduced into the high boiling point fraction separation column 1.

The vaporizer 4 of the high boiling point fraction separation column 1 is charged with the hot reaction product of a direct chlorination plant. The vapor line 15 of the high boiling point fraction separation column 1 branches into the line 16 to the condenser 5; the condensate formed here is collected in the 1,2-dichloroethane reservoir 12. The reflux from the high boiling point fraction separation column 1 is fed from the 1,2-dichloroethane reservoir 12 via the line 17 to the head of the high boiling point fraction separation column. The sump product, which contains the high boiling point fraction, flows through the drain line 18 into the vacuum column 3 (vacuum distillation zone).

From the vapor line 15, an additional vapor line 19 branches off to the vaporizer 7 of the vacuum column 3; the condensed vapors flow in the form of condensate via the drain line 20 into the 1,2-dichloroethane reservoir 12. From the vacuum column 3, the sump product which contains the high boiling point fraction is transferred outward via the sump line 21 into a combustion phase. The vapors from the vacuum column 3 flow through the head line 22 into the condenser 9; a portion of the condensate formed flows through the return line 23 in the form of the return into the vacuum column 3, and the rest of the condensate is discharged through line 24 in the form of pure 1,2-dichloroethane and fed via line 36 to a 1,2-dichloroethane cracking plant.

Wet, crude 1,2-dichloroethane from an oxychlorination process is fed into the dehydration column 2 via the input line 25. The vapors from the dehydration column 2 flow via the azeotrope line 26 into the condenser 8; the condensate formed flows through line 27 into the separation container 10, in which an aqueous phase is deposited on a 1,2-dichloroethane phase. The aqueous phase is transferred outward via the discharge line 28. The 1,2-dichloroethane phase that contains the low boiling fractions (ratio of 1,2-dichloroethane : low boiling fractions = 1:1) from the separation

container 10 is returned to the head of the dehydration column 2 via the return line 29. The low boiling fractions are transferred outward via the extraction line 30. From the vapor line 15 of the high boiling point fraction separation column 1, an additional vapor line 31 branches off into the compressor 11. The compressed vapors flow via line 32 into the vaporizer 6 of the dehydration column 2; the condensate formed is discharged through the line 33, choke 34 and line 35 into the 1,2-dichloroethane reservoir 12. The purified 1,2-dichloroethane is discharged from the 1,2-dichloroethane reservoir 12 through the line 17 into the 1,2-dichloroethane feed container 43. 1,2-dichloroethane from the direct chlorination process is fed into the 1,2-dichloroethane feedback container 43 and combined with the purified 1,2-dichloroethane from the 1,2-dichloroethane reservoir, and transported together via the product line to a 1,2-dichloroethane cracking plant.

In one variation of the method claimed by the invention, excess vapor heat can be fed downstream of the compressor 11 via the line 38 to the vaporizer of a hydrochloric acid distillation column 39, in which hydrochloric acid is separated from the liquefied cracked gas of the thermal 1,2-dichloroethane cracking; the condensate formed then flows through line 40, choke 41 and line 42 into the 1,2-dichloroethane reservoir 12.

An additional advantage of the method claimed by the invention is that the content of 1,1,2-trichloroethane in the pure 1,2-dichloroethane is lower, because at a lower distillation temperature, less gaseous 1,1,2-trichloroethane is distilled via the head. 1,1,2-trichloroethane is a substance that promotes the cracking of 1,2-dichloroethane into elementary carbon and thus leads to a carbonization of the cracking tube. Therefore the 1,2-dichloroethane vapors from the high boiling point fraction column described in EP-B-01 80 925 contain approximately 300 parts by weight 1,1,2-trichloroethane, while in the method claimed by the invention, the 1,2-dichloroethane vapors contain 100 to 200 parts by weight 1,1,2-trichloroethane.

Example

13,930 kg/h of crude 1,2-dichloroethane from the cracked gas processing and 9,790 kg/h of crude dehydrated 1,2-dichloroethane from column 2 are fed into the high

boiling point fraction separation column 1. The sump temperature of the column 1 was 110°C, the vapor temperature 100°C. The column 1 was operated at a reflux ratio of $R = 0.5$. The sump product was transferred into the column 3. In the vacuum column 3, the sump temperature was 88°C and the boiler pressure 0.4 bar; the head temperature was 45°C at a pressure of 0.26 bar.

The vacuum column 3 was operated at a reflux of $R = 0.5$. 336 kg/h of sump product was extracted from the vacuum column 3.

9,990 kg/h of wet 1,2-dichloroethane from an oxychlorination plant was introduced into the dehydration column 2. In the dehydration column 2, a sump temperature of 105°C was measured, a head temperature of 82°C, a boiler pressure of 1.9 bar and a head pressure of 1.4 bar.

40 kg/h water and 75 kg/h of low boiling fractions were extracted together with 70 kg/h 1,2-dichloroethane from the separation container 10. In the 1,2-dichloroethane feed container 43, 4670 kg/h of 1,2-dichloroethane via line 24 and 18,719 kg/h of 1,2-dichloroethane from the 1,2-dichloroethane reservoir 12 were combined via line 17 and dispensed jointly via line 36 into a 1,2-dichloroethane cracking plant.

The vaporizer 4 of the high boiling point fraction separation column 1 (high boiling point fraction separation zone) was charged with 830,000 kg/h of 1,2-dichloroethane at a temperature of 125°C from a direct chlorination.

A first vapor flow of 1,900 kg/h was condensed in the condenser 5.

A second vapor flow of 10,110 kg/h was condensed in the vaporizer 7 of the vacuum column 3 (vacuum distillation zone).

A third vapor flow of 15,990 kg/h was compressed to a pressure of 3.2 bar at a temperature of 127°C. 11,600 kg/h of this compressed vapor flow was condensed in the vaporizer 6 of the dehydration column 2 (dehydration zone). 4330 kg/h of the compressed vapor flow was condensed in the vaporizer of a column 39 (hydrochloric acid distillation zone), the sump temperature of which was 99°C. The condensate of the vaporizer of the column 39 flowed through line 40, choke 41 and line 42 into the 1,2-dichloroethane reservoir. The 1,2-dichloroethane that collected in the 1,2-dichloroethane reservoir 12 contained 120 parts by weight of 1,1,2-trichloroethane.

Claims

1. Method for the utilization of the heat of 1,2-dichloroethane vapors as they occur in a high boiling point fraction separation zone in which the high boiling point fractions are extracted in liquid form from crude 1,2-dichloroethane in the form of a mixture with 1,2-dichloroethane, and the crude 1,2-dichloroethane in dehydrated form originates from a dehydration zone of an oxychlorination plant and from a vinyl chloride distillation zone of a 1,2-dichloroethane cracking plant for the production of vinyl chloride, **characterized in that** the vaporizer of the high boiling point separation zone is operated with the reaction enthalpy of the direct chlorination of ethylene to 1,2-dichloroethane and divides the 1,2-dichloroethane vapors into 3 gas streams:

- a) a first gas stream is transported to the vaporizer of a vacuum distillation zone, in which 1,2-dichloroethane is separated from high boiling point compounds, and the condensate that is formed in the vaporizer is collected in a 1,2-dichloroethane reservoir;
- b) a second gas stream leads into a condensation zone and the condensate formed collects in the 1,2-dichloroethane reservoir;
- c) a third gas stream is compressed in a compression zone and in this state is fed to a vaporizer of the dehydration zone in which low boiling point compounds and water are added to the 1,2-dichloroethane from oxychlorination plants and the condensate that is formed collects in the 1,2-dichloroethane reservoir.
- d) optionally, from the third gas stream, downstream of the compression zone, a partial gas stream branches off into the vaporizer of a hydrochloric acid distillation zone in which hydrochloric acid is distilled from a mixture of vinyl chloride and 1,2-dichloroethane.

2. Method as recited in Claim 1, characterized in that the sump of the high boiling point fraction separation zone is set at a temperature of 95 to 120°C and a vapor temperature of 84 to 112°C.

3. Method as recited in one of the Claims 1 and 2, characterized in that the 1,2-dichloroethane vapors of the third gas stream are compressed to a pressure of 2 to 4.5 bar, whereby a temperature of 110°C to 150°C is established.
4. Method as recited in one of the Claims 1 to 3, characterized in that 3 to 15%, in particular 5 to 10%, of the 1,2-dichloroethane vapors are condensed in the condensation zone.
5. Method as recited in one of the Claims 1 to 4, characterized in that a reflux of $R = 0.2$ to 0.8 , in particular of $R = 0.4$ to 0.6 , is established in the high boiling point fraction separation zone.
6. Method as recited in Claim 1, characterized in that from the sump product of the high boiling point fraction separation zone, the high boiling point fraction is extracted from the boiler of the vacuum distillation zone at a sump temperature of 75 to 100°C and a boiler pressure of 0.25 to 0.6 bar.
7. Method as recited in Claim 1, characterized in that dehydrated crude 1,2-dichloroethane is extracted from the boiler of the dehydration zone at a sump temperature of 95 to 115°C and a boiler pressure of 1.5 to 2.5 bar and introduced into the high boiling point fraction separation zone.

1 page of drawings